

DIFFERENTIAL SCANNING CALORIMETRY OF VOLATILE-BEARING IRON MINERALS UNDER MARS-LIKE PRESSURES: NEW INSIGHTS INTO ENERGETICS AND MECHANISMS OF THERMAL DECOMPOSITION. I- C. Lin¹, H. V. Lauer Jr.², D. C. Golden², and D. W. Ming¹, ¹NASA Johnson Space Center, SN2, Houston, TX 77058 (i-ching.lin1@jsc.nasa.gov), ²Lockheed-Martin SMS&S, 2400 NASA Rd1, Houston, TX 77058.

Introduction: Searching for hydrated iron oxides, carbonates and clays on Mars has been a focus of the Mars Surveyor Program. Finding such volatile-bearing minerals may indicate the past presence of a warm, wet Martian environment that could have supported life. The Thermal and Evolved-Gas Analyzer (TEGA) instrument, which was a part of the Mars Polar Lander payload, was to perform calorimetry and evolved-gas analysis on soil samples collected from the Martian surface.

By investigating thermal reactions of substances, it is possible to not only identify their constituents, but also study their physical and chemical properties. Thermodynamics of a phase transition is a function of the pressure (P) and temperature (T). However, the phase boundary is not simply a straight line, since entropy change and volume change are not independent of P and T. For reactions involving volatiles (e.g., H₂O and CO₂), phase boundaries are strongly curved in P-T space, because the volume of the volatile phase depends very strong on P and T. In order to successfully interpret the TEGA data, we have investigated a series of Mars analog volatile-bearing minerals at reduced atmospheric pressures [1].

In this study, we have examined the thermal decomposition of two volatile-bearing iron minerals, in particular, lepidocrocite (γ -FeOOH) and siderite (FeCO₃), under Mars-like pressures. Both minerals exhibit different enthalpic events during their decomposition at reduced atmospheric pressures when compared to those at ambient pressure. These differences in energetics are related to the mechanisms of thermal decomposition at Mars-like pressures. Such knowledge regarding the thermal stability of volatile-bearing minerals on Mars will provide useful information for planetary surface processes.

Experimental: We used a well-characterized synthetic lepidocrocite and a pure natural siderite for this study. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7, which was modified to conduct reduced pressure experiments [2,3]. Calibration was done by a "simultaneous" calibration method. This method, by putting three metal standards and one sample into a four-spoke DSC crucible, allows an efficient way to calibrate both enthalpy and temperature for each single run. This cali-

bration method is especially suitable for our experiments when various pressures (1, 0.1, and 0.01 bar) were encountered, because pressure substantially affects the thermal characteristics of calorimeter. The DSC experiments were carried out at a heating rate of 20°C/min under flowing N₂.

Results and Discussion: Upon heating, lepidocrocite shows two thermal events, which result in relatively broad peaks compared to the melting of metal standards. The endothermic peak around 250°C is due to the loss of the water, i.e. dehydroxylation, and lepidocrocite becomes maghemite (γ -Fe₂O₃). The exothermic peak around 450°C is a phase transition from maghemite to hematite (α -Fe₂O₃) (see Figure 1).

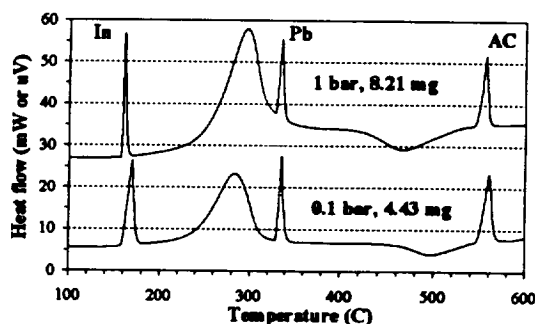


Figure 1. DSC scans for lepidocrocite

Siderite only undergoes an endothermic transition during heating. This broad transition around 500°C is related to the decarbonation of siderite and the oxidation of decarbonated iron oxides (see Figure 2).

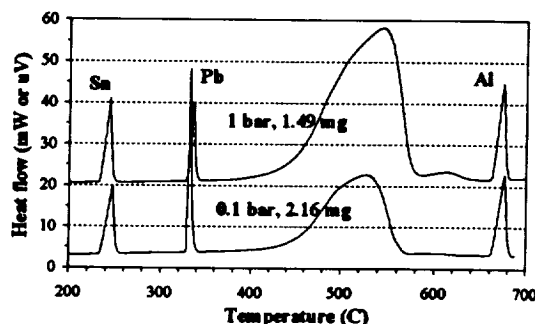


Figure 2. DSC scans for siderite

Wustite (FeO) and magnetite (Fe₃O₄) were found in

the final product; the phase that formed depended on the amount of oxygen available in the system. Preliminary results on enthalpies of these thermal events are listed in Tables 1 and 2.

Lepidocrocite: free expansion of water. The enthalpy of dehydroxylation increases as the pressure decreases from 1 to 0.01 bar. The difference in enthalpies is nearly equal to the work needed to expand water from higher pressure to lower pressure (Table 1).

Table 1. Enthalpy of Lepidocrocite Dehydration.

Pressure	KJ/mol	Error	Difference	KJ/mol	$W=nRT\ln(P1/P2)$
1 bar	34.17	1.35	1-0.1	4.67	4.72
0.1 bar	38.84	0.83	0.1-0.01	4.75	4.72
0.01 bar	43.59	1.70	1-0.01	9.42	9.44

Because of lepidocrocite's open layered structure, water ideally expands within the framework of lepidocrocite during its dehydroxylation at reduced atmospheric pressures. This finding also supports that the dehydroxylation precedes the structural conversion to maghemite [4].

Siderite: easier route for CO₂ evolution. Our data indicates a larger endothermic peak for the decarbonation at ambient pressure when compared to reduced pressure conditions. After examining many possible reactions in the system, the huge difference in enthalpies due to different pressures can only be equalized with the magnitude of dissociation of carbon dioxide to carbon monoxide (Table 2). Carbon mon-

Table 2. Enthalpy of Siderite Decarbonation.

Pressure	KJ/mol	Error	Difference	Dissociation of CO ₂
1 bar	529.45	NA	301.37	285 (kJ/mol)
0.1 bar	228.08	23.15		

oxide was later detected during an ambient pressure experiment using infrared spectroscopy, while no carbon monoxide was observed during reduced pressure DSC runs. The decarbonation is a topochemical process rather than an intracrystalline dissociation. For the reaction to proceed from the surface towards the center of the crystal, it is necessary that CO₂ be capable of diffusing through the crystal structure. The pressure surrounding the crystal must be an important factor for such a diffusion process. At reduced pressures, because the pressure difference inside and outside the crystal is greater, CO₂ can be driven out the structure without further dissociation. That is, CO₂ evolving out of the crystal lattice is enhanced by the pressure gradient from inside the structure to the surround atmosphere. At ambient pressure, because of a smaller pressure gradient, CO₂ further dissociates to CO inside the

crystal lattice in order to process the decarbonation, allowing only CO to diffuse out the crystal. The oxygen ion dissociated from CO₂ within the crystal lattice also provides a convenient source for the oxidation of iron oxides. Thus, the decarbonation of siderite is a simpler and less energetic process under reduced atmospheric pressure.

Maghemite is a metastable phase, that converts to hematite during the heating of lepidocrocite. The temperature range for maghemite is extended at reduced pressures, as the exothermic transition moves towards higher temperature (Figure 1). In other words, maghemite becomes more stable relative to hematite at lower atmospheric pressure. This supports that the stability of metastable phases (e.g., glasses) with a positive dP/dT of melting will be greater at reduced atmospheric pressures [5]. Additional experiments are currently in progress to refine the energetics relating the thermal decomposition of lepidocrocite and siderite.

Conclusions: At Mars-like pressure, the dehydroxylation of lepidocrocite, which has an open layered crystal structure, is more endothermic. The extra energy is required to allow the water to expand ideally within the crystal at reduced atmospheric pressures. On the other hand, the decarbonation of siderite is a less endothermic process under Mars-like pressure. The lower atmospheric pressure may result in a greater pressure gradient for the pathway of diffusion and facilitate the carbon dioxide diffusing through the lattices without further being dissociated into carbon monoxide.

References: [1] Lauer Jr. H. V. et al. (2000) *LPS XXXI* CD-ROM. [2] Golden D. C. et al. (1999) *LPS XXX* CD-ROM. [3] Lauer Jr. H. V. et al. (1999) *LPS XXX* CD-ROM. [4] Gehring A. U. and Hofmeister A. M. (1994) *Clays & Clay Miner.*, 42, 409-415. [5] Lin I-C. (1997) Ph.D. thesis, Princeton University.